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TECHNOLOGICAL PARTICULARS AND PROPERTIES OF TITANIUM-CONTAINING CRYSTAL GLASS

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A composition is proposed for titanium-containing crystal glass with high chemical stability, heat resistance and hardness. The glassmaking process is studied under laboratory conditions. To prevent iron-titanium chromophoric groups from coloring the glass it is recommended that raw material of very high purity, specifically, enriched quartz sand and enriched vein quartz of very high quality, be used. The glass is safe to produce and use.

Key words: crystal, safety, glass formation, decoloration, chemical stability, hardness, efficiency.

The demand for glassware in Russia increases every year. BusinesStat expects this trend to remain in the future. For example, the retail sales volume of glassware is expected to reach 614×10^6 units in 2016, which is 1.3 times higher than in 2011.

As the assortment and functionality of glassware increase the safety requirements for production and operation become more stringent.

In the current situation a truly revolutionary breakthrough is the development and production of a new type of lead-free crystal glass, called Tritan®, by the German company Schott Zwiesel. Like lead crystal, Tritan® is transparent, chemically stable, strong, hard and completely safe to use.

The current technical standard GOST 24315–80 "Glassware and Decorative Glass Articles: Terms and Definitions of Glass Types, Methods of Production and Decoration" in Russia defines crystal glass as a colorless silicate glass with mass content of the oxides PbO, BaO, ZnO and K_2O separately or in combination at least 10% and it classes low-lead, lead, high-lead and barium glass, containing 18 to 30% or more of the oxides PbO and BaO, respectively, as crystal glass. The production of lead crystal glass and the use of crystal glassware raise numerous environmental, worker safety and health issues [1 – 3].

At the same time, according to [4, 5] titanium dioxide greatly increases (like and even more so than PbO) the index of refraction and reflectance of the glass while increasing chemical and heat resistance, decreasing the proneness to crystallization and viscosity of the molten glass and the melting temperature, which characterizes it as a very valuable component of crystal glass.

It should be noted that not all specialists attach the same value to an increase in the hardness of crystal glass. For example, in RB patent No. 10999 'Colorless crystal glass' low values of the microhardness of crystal (3000 – 3500 MPa) are evaluated positively as a factor greatly facilitating machining (cutting, grinding, faceting, etching), while hardness and scratch resistance are considered to be important attributes of Tritan® glass.

The coloration of titanium-containing glass can also be problematic. It is well known [4, 6] that in the absence of transitional elements (Fe^{2+}, Fe^{3+}) titanium-containing glasses are colorless. A number of researchers consider Fe^{3+} (Fe^{2+}) ions to be responsible for the color of titanium-containing glass; under the strong polarizing force of Ti^{4+} they transition from the position of a modifier [FeO_6] into the position of a network former [FeO_4]. In this case the chromophoric centers responsible for the shift of the absorption edge into the long-wavelength region and for the color of the glass can be represented as iron-titanium complexes in which Fe^{2+}–O–Ti^{4+} or Fe^{3+}–O–Ti^{4+} bonds are formed. Thus, the interaction of titanium and iron is the main factor determining the color of glass. In [4] it is also noted that an increase in the basicity of glass sharply decreases the intensity of the color, shifting the absorption edge into the short-wavelength region. For the ratio $Na_2O/TiO_2 > 1$ glass with iron impurities is very weakly colored even with high TiO_2 content.

On this basis it is of interest to investigate the technology and properties of titanium-containing glass for glassware.

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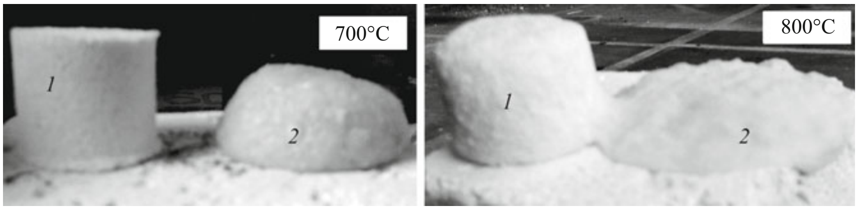

Fig. 1. Exterior view of briquettes of the batches for titanium (*1*) and lead (*2*) crystal after heat treatment.

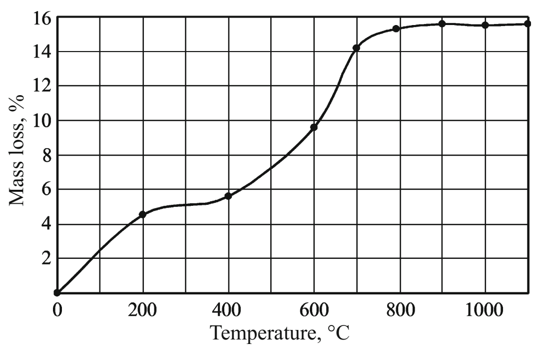

Fig. 2. Batch losses during heat treatment.

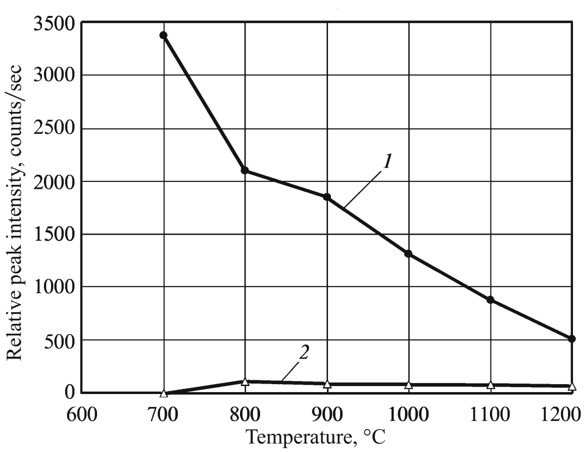

Fig. 3. Variation of the intensity of the quartz peaks $d = 3.343$ Å (*1*) and cristobalite $d = 4.077$ Å (*2*) in the x-ray diffraction patterns of the products of heat treatment of batch. Treatment time: 1 h.

We have developed a multicomponent composition that is highly prone to glass formation and makes it possible to obtain the required complex of production and performance characteristics. The oxides TiO_2 and ZrO_2 are introduced in order to increase the refractive index; they also increase the mechanical properties, water resistance, acid resistance (TiO_2), alkali-resistance (ZrO_2) and heat resistance. Since zirconium dioxide increases the viscosity of glass and the glassmaking temperature, its mass content was limited to 4% and the TiO_2 content was taken to be a factor of 2 higher — 8%.

TABLE 1. Working Properties of Alternative Crystal Glasses

Property	Lead crystal	Titanium-containing crystal glass
Density ρ, kg/m^3	2947.1	2766.6
Average dispersion Δn	1181.9×10^{-5}	1153.7×10^{-5}
Refractive index n_D	1.5525	1.5592
Elastic modulus E, GPa	61.3	73.1
Shear modulus G, GPa	24.4	29.7
CLTE, $10^{-7} \times K^{-1}$	102.8	82.3

The alkali oxides are represented by Na_2O and K_2O in the ratio 1 : 2 with total amount 15%. Such proportions will lower the melting temperature and the temperature gradient of the viscosity and secure the two-alkali effect in regards to water resistance. In addition, a significant amount of alkali oxides is a necessary condition for the cations Ti^{4+} and Zr^{4+} to be in tetrahedral coordination and incorporated into the glass network. A high content of alkali oxides will also ensure destruction of chromophoric groups and decoloration.

To suppress possible coloring by iron sulfides ZnO is introduced into the glass; it also significantly increases the water resistance and mechanical properties but not the glass viscosity or glassmaking temperature.

Aluminum oxide was introduced into the glass in order to suppress phase separation — liquation and crystallization. In addition, Al_2O_3 increases the mechanical properties, heat resistance and chemical stability.

In summary, a safe glass composition, which is as good as lead crystal while surpassing the latter in regards to the mechanical, chemical and thermal characteristics, was designed for the experimental studies (Table 1).

The following were used for the batch: OOVS-015-1 quartz sand (GOST 22552–77), alumina, titanium and zinc white pigment, zirconium oxynitrate dihydrate $ZrO(NO_3)_2 \cdot 2H_2O$, soda, potash and saltpeter as well as arsenic trioxide as a chemical decolorant and clarifier for the molten glass. On the basis of the batch the glass yield was 88.8% and the batch loss 11.2%.

The batch for titanium-containing glass is more refractory than the batch for lead crystal from the Dyat'kovo Crystal Works (Fig. 1).

Batch losses are recorded on heating to 900°C. At low temperatures (300°C) they are due to the removal of the physical and hydrate water, while above this temperature they are due to the decomposition of nitrates and carbonates (Fig. 2).

The amount of free quartz in the products of heat treatment (Fig. 3) decreases considerably (according to x-ray phase analysis) as the batch is heated in steps to 1200°C. This is promoted on the one hand by reactions leading to the

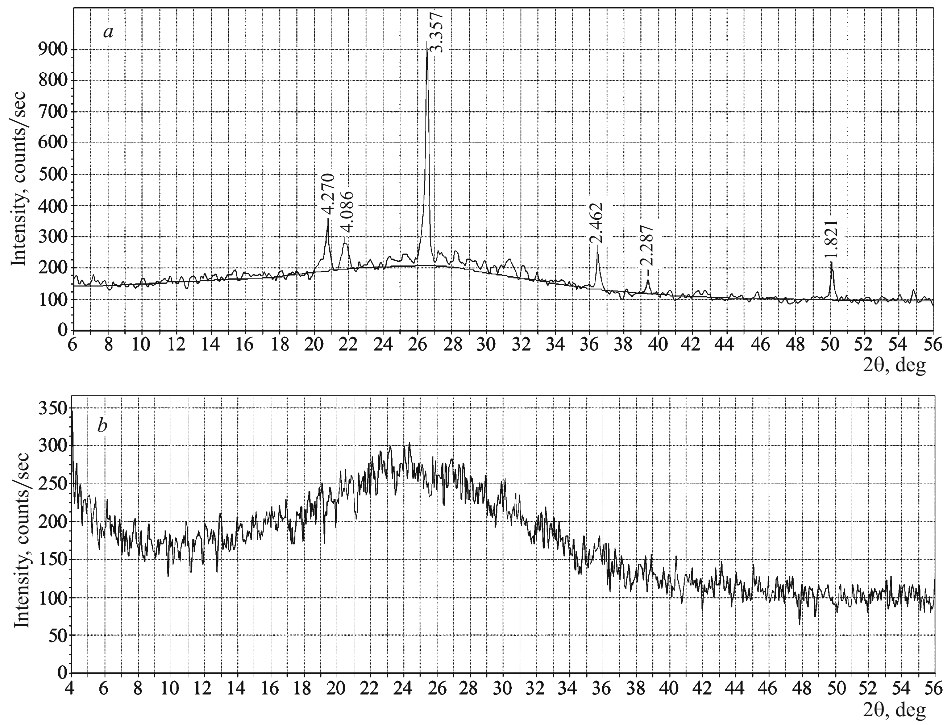

Fig. 4. X-ray diffraction patterns of the products of heat treatment of batch at 1000°C (*a*) and 1350°C (*b*).

formation of silicates and on the other by a process of gradual dissolution of quartz in the primary silicate melt. Polymorphic transformations of quartz with formation of cristobalite intensify both processes.

An amorphous halo is recorded in the x-ray diffraction patterns starting at 900°C. The halo becomes distinct at 1000°C (Fig. 4*a*). Heat treatment of batch for 3 h at 1350°C resulted in the completion of the glass formation process — peaks due to residual quartz are completely absent in the x-ray diffraction pattern (Fig. 4*b*). However, the surface of the glass was covered with the glassmaking foam and the bubble content was about 8 – 9 vol.%.

In the laboratory titanium-containing crystal glass was made in an electric resistance furnace with Silit heaters, using 150 and 300 ml crucibles with soaking at 1450°C for 2 h. The crucibles with the molten glass were cooled and heated in the furnace; the glass was used to determine the properties. It should be noted that in the absence of convective motion, mixing and churning in the molten glass small striae and fine seeds were observed in the glass.

The refractive index of the glass, determined by the immersion method, was 1.555. This corresponds to the classification of crystal.

In regards to water resistance the composition of the titanium-containing glass greatly surpassed lead crystal. The fast GIS method shows the glass to be of the hydrolytic class (0.5 – 0.6 ml 0.01 N HCl and 2.6 – 2.7 ml for lead crystal). The high water resistance is due to titanium, zirconium and zinc oxides as well as the presence of two alkaline oxides — Na_2O and K_2O (double alkali effect). The chemical resistance of glass intended for glassware is extremely important.

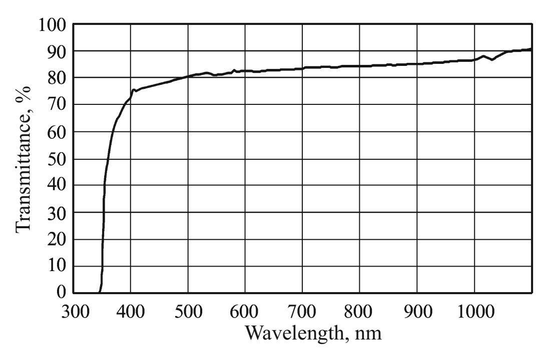

Fig. 5. Spectral light transmission of glass (sample thickness 3 mm).

The microhardness of the glass surface was 5400 – 5500 MPa, which corresponds to the hardness of sheet and container glass and makes articles highly stable in automatic dish-washing machines and prevents surface abrasion and scratches. At the same time this level of hardness makes it possible to implement methods of machining and decoration of articles such as grinding, etching, diamond faceting, wide-plane faceting and sandblasting. From our standpoint high surface hardness of glass articles is a positive quality, especially with the current trend toward using articles made of smooth glass.

The spectral light transmission was determined with a SF-56 automatic spectrophotometer in the wavelength range from 300 to 1100 nm with data recorded every 10 nm (Fig. 5). The coordinates of the *RGB* diagram were determined according to the dependence $T = f(\lambda)$ obtained: $x = 0.3175$, $y = 0.3257$, which is very close to the coordinates x, y of the point corresponding to the color white — 0.33, 0.33.

The multicomponent glass composition developed for glassware and studied under laboratory conditions is harmless, possesses useful technological characteristics and a range of valuable operating properties and can be recommended for industrial testing.

Its most valuable properties — extremely high chemical stability, heat resistance, mechanical strength and hardness — make it suitable for glassware of different kinds and give a long service life under modern conditions.

A necessary condition for obtaining high-quality colorless glass is guaranteed purity of the raw materials, first and foremost, raw quartz. It is recommended that OOVS-010-V sand (GOST 22551–77) or quartz gangue obtained from vein quartz be used.

Industrial approval of the proposed composition of titanium-containing crystal glass entails a more careful formulation of the recipe of auxiliary raw materials as well as intensification of the glassmaking process (increasing the melting temperature to at least 1480 – 1500°C, mixing, churning the molten glass) in order to obtain glass with high homogeneity.

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